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(71) Applicant: 591030983

Head of the National Institute for Research in Inorganic Materials
1 Namiki 1-chome
Tsukuba-shi, Ibaraki-ken

(72) Inventor: Takayasu IKEGAMI
2-908-103 Atsuma
Tsukuba-shi, Ibaraki-ken

(72) Inventor: Yusuke MORIYOSHI
8-2-27 Kinuta
Setagaya-ku, Tokyo-to

(54) [Title of the Invention] Method for
Fixation of CO₂ by Alkaline Earth
Silicate

(57) [Abstract]

[Problem] The problem of this invention is to provide a new method for fixation of CO₂ (thought to be one factor of global warming) that fixes CO₂ by an alkaline earth silicate, and furthermore, this method is capable of simultaneously producing fine spherical silica inexpensively and in high volume.

[Means to Solve the Problem] A powder, comprising at least 1 member of a group consisting of calcium silicate and magnesium silicate, is suspended in water. CO₂ or CO₂-containing gas is blown into the aqueous suspension in a fluidized state to cause reaction of the gas.



[Scope of the Patent Claims]

[Claim 1] A method for fixation of CO₂ by an alkaline earth silicate comprising the steps of: suspending in water of a powder comprising at least 1 member of a group consisting of calcium silicate and magnesium silicate, and causing reaction in the fluidized state by blowing CO₂ or CO₂-containing gas into the aqueous suspension.

[Claim 2] The fixation method according to claim 1, wherein particle size of the powder is less than or equal to 50 mesh.

[Claim 3] The fixation method according to claim 1, wherein liquid is fluidized at least sufficiently strongly so that powder does not precipitate out.

[Claim 4] The fixation method according to claim 1, wherein the substance containing calcium silicate or magnesium silicate is subjected to preparatory heating treatment.

[Claim 5] The fixation method according to claim 1, wherein temperature of the suspension solution is greater than or equal to 30°C.

[Claim 6] The fixation method according to claim 1, wherein a substance generating acidity or basicity is added to the aqueous suspension, and CO₂ or CO₂-containing gas is blown into the aqueous suspension.

[Claim 7] A method for production of fine spherical silica, wherein fine spherical silica is produced and obtained during the CO₂ fixation method according to any one of claims 1 through 6.

[Detailed Description of the Invention]

[0001]

[Technical Field Relating to the Invention] This invention relates to a method for fixation of CO₂ by an alkaline earth silicate. Furthermore, this invention particularly relates to a method for fixation of CO₂ (thought to be one factor in global warming) by fixation of CO₂ by an alkaline earth silicate by a method that is useful also for the production of fine spherical silica.

[0002]

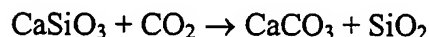
[Conventional Technology] In recent years, CO₂ has come to be considered to be one factor in global warming, and a major environmental problem needing to be solved by humanity has become the fixation and removal of CO₂ from the atmosphere. Candidate methods that have been considered presently for the effective fixation of CO₂ include: methods for synthesis of organic substances (e.g., methanol and the like) by reaction of CO₂ and H₂; methods for using CO₂ in artificial photosynthesis; methods for disposal by increasing concentration and liquefaction of CO₂ and injecting into the deep sea; methods of disposal of CO₂ by compression and storage within the earth in depleted oil fields, gas fields, etc.; and the like.

[0003] However, treatment costs of all of these methods are high, resulting in a high economic burden. Also practical problems remain for deep sea disposal due to the danger of adverse effects

of CO₂ on the environment. Moreover, the methods of fixation as carbonates are being investigated as technologically simple methods. One such method causes adsorption by hydroxides of an alkali metal or alkaline earth metal. However, a large quantity of energy is required for synthesis of this type of hydroxide, and this method is deficient in that CO₂ is generated in order to obtain such energy. Furthermore, causing adsorption by use of the reaction of Urey (Urey) on a silicate mineral containing calcium and magnesium has been suggested as another method. The reaction formulae are indicated below.

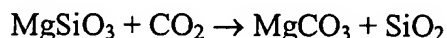
[0004]

[Reaction 1]



[0005]

[Reaction 2]



However, this reaction has been proposed based on geochemical research, and this reaction proceeds over a time span on the order of several hundred years during generation of rock. It has thus come to be thought that a technical breakthrough would be necessary for practical application of this reaction. However, fixation of CO₂ by the above mentioned reactions has been also considered from another standpoint. That is to say, this reaction generates silica (SiO₂).

[0006] Silica is not simply used, as earlier, as a ceramic material. Silica has received attention as a new material in recent years due to chemical resistivity, heat resistance, low thermal expansion, electrical resistance, optical properties, and the like. This type of silica, for example, is manufactured industrially as fine silica by methods such as: a method of dissolving silica sand and sodium carbonate at 1200°C to 1300°C to form sodium silicate and then adding a mineral acid (sulfuric acid and the like) to this sodium silicate, a method of adding an alkaline earth metal to sodium silicate and then adding a mineral acid, a method of adding an organic solvent to a gel produced by reaction between sodium silicate and a mineral acid and then thermally decomposing the resultant organo-gel, a method of adding a mineral acid to activated white clay, and the like. Moreover, methods that have been proposed recently for production of high purity product are: a method of thermally decomposing silicon tetrachloride in the presence of hydrogen and oxygen, a method of thermally decomposing a metal alkoxide, and the like.

[0007] However, these earlier production methods are deficient in that numerous steps are required, and this itself results in high cost. Moreover, the silica produced by these methods forms secondary particles due to agglomeration of multiple fine particles, and this is disadvantageous in that there is a worsening of blending performance and dispersion. Therefore the object of this invention is to solve the above described deficiencies and limitations of the conventional technology by providing a new method for making possible fixation of CO₂ (thought to be one factor of global warming) while simultaneously producing fine spherical silica inexpensively and in high volume.

[0008]

[Means to Solve the Problem] This invention provides a method for fixation of CO₂ by an alkaline earth silicate by suspending in water a powder comprising at least 1 member of a group consisting of calcium silicate and magnesium silicate, and causing reaction in the fluidized state by blowing CO₂ or CO₂-containing gas into the aqueous suspension.

[0009] Furthermore, in addition to fixation of CO₂ by the above mentioned alkaline earth silicate, this invention also provides a method for manufacture of fine spherical silica.

[0010]

[Embodiment of the Invention] The CO₂ targeted for fixation by this invention is not particularly limited with respect to origin or source of supply of such, and the target of this invention also includes CO₂ or CO₂-containing gas discharged by industrial production or consumption of fossil fuel. The calcium silicate prescribed for this invention is taken to be a generic term for a formulation of chemical compounds combining calcium oxide and silicon dioxide, and thus there may be various proportions of these components. Moreover, no particular limitation is placed on the chemical substance mainly comprising calcium oxide and silicon dioxide, even if chemical species such as the hydroxide group and the like are bonded thereto, as long as the chemical substance exhibits the characteristics of this invention. This occurs naturally as wollastonite (CaSiO₃) and di-calcium silicate (CaSiO₄) [*sic*]. Wollastonite is the form that is mostly used industrially, and this is used for applications such as a ceramic ware raw material, tile raw material, electrical ceramic, flux for welding rods, and the like. However, the amount utilized as raw material is still low, and there is a need for the development of applications. Moreover, in addition to the natural mineral, it is possible to use cement or steel, di-calcium silicate contained in low-bubble content concrete, tri-calcium silicate, tobermorite, and the like.

[0011] Moreover, the magnesium silicate prescribed by this invention is taken to be a generic term for a formulation of chemical compounds combining magnesium oxide and silicon dioxide, and thus there may be various proportions of these components. Moreover, no particular limitation is placed on the chemical substance mainly comprising magnesium oxide and silicon dioxide, even if chemical species such as the hydroxide group and the like are bonded thereto, as long as the chemical substance exhibits the characteristics of this invention. This occurs naturally and is in abundant supply as olivine, serpentine, talc, chlorite, asbestos (asbestos), and glauconite. Although asbestos is used widely in industry, carcinogenicity of asbestos has become a problem in recent years. In addition to the problem of suppressing the use of asbestos, detoxifying treatment of waste from previously used asbestos has become a problem. This invention can also utilize construction materials containing asbestos. This invention is capable of utilizing a mixed compound or solid substance that contains at least this calcium silicate and/or this magnesium silicate.

[0012] Furthermore, particle size of the powder of the substance (that contains at least 1 member of the group consisting of calcium silicate and magnesium silicate) is as small as possible in order to accelerate the reaction with CO₂. Surface area is preferably high, and particle size is preferably less than or equal to 50 mesh. Although as fine a size as possible is of course preferred, since the energy required for pulverization increases as particle size becomes smaller,

in practice the particle size must be determined while considering the energy required for pulverization. Moreover, reaction rate can be greatly accelerated by use of the fluidized state for the suspension solution. Fluidization velocity is preferably as high as possible, and the liquid is preferably fluidized at least strongly enough so that the powder does not precipitate out. Furthermore, as may be required, the reaction can be promoted by preparatory heating treatment of the substance containing calcium silicate or magnesium silicate.

[0013] Furthermore, addition of a substance generating acidity or basicity to the aqueous suspension and blowing CO₂ or CO₂-containing gas into the aqueous suspension is disclosed as one aspect of this invention. The acid-generating chemical substance for the aqueous suspension is exemplified by mineral acids (hydrochloric acid, nitric acid, sulfuric acid, and the like) or organic acids and the like. Such substances increase the dissolved concentration of calcium ion or magnesium ion in the aqueous solution. Generally the chance of collision between ions increases, and reaction rate increases, as ion concentration increases. According to this principle, the acid-generating chemical substance promotes the reaction between CO₂ and the substance that contains calcium silicate or magnesium silicate. For this reason, no particular limitation is placed on the type of this chemical substance as long as the chemical substance acts in the above mentioned manner. Moreover, the upper limit of the concentration of the chemical substance is the concentration of a saturated aqueous solution. Although no particular limitation is placed on the lower limit of concentration, the reaction rate slows as this concentration decreases, and thus the concentration is preferably at least 0.1%. The reaction rate of a system that contains magnesium silicate is low, and thus a concentration greater than or equal to 0.5% is preferred. Generally the exhaust gas is not simply CO₂, but rather is a mixture with sulfur dioxide gas, chlorine gas, nitrogen oxides, and the like. These gases are preferably used since these gases produce acidity when dissolved in water. Furthermore, when such gas is blown into the water of the suspension of the substance that contains calcium silicate or magnesium silicate, non-addition of a chemical substance especially to generate acid is also permissible.

[0014] Chemical substances for generation of basicity in the aqueous suspension are exemplified by sodium hydroxide, potassium hydroxide, and the like. Although ammonia is also a chemical substance that generates basicity, ammonia is undesirable due to volatilization and loss from the aqueous solution at high temperature. These substances increase the solubility of silica in the aqueous solution and are used for promoting the reaction between CO₂ and the substance containing calcium silicate or magnesium silicate. The upper limit of concentration is the concentration of a saturated solution in water. Although no particular limitation is placed on the lower limit of concentration, the reaction rate slows as this concentration decreases, and thus the concentration is preferably at least 0.1%.

[0015] The reaction of this invention between CO₂ and the substance that contains at least calcium silicate and / or magnesium silicate proceeds according to the above mentioned reaction of Urey (Urey). This reaction proceeds sufficiently in the vicinity of room temperature due to the fine size of the powder and due to addition to the system of the chemical substance that generates acidity or alkalinity. However, the reaction rate increases with increasing temperature, and the temperature of the suspension solution is preferably greater than or equal to 30°C. Since temperature of CO₂-containing exhaust gas discharged from a factory is normally 100°C to

200°C, there is no particular need for heating the suspension solution if such exhaust gas is utilized. However, when high temperature exhaust gas is blown in continuously, water is preferably fed as required in accompaniment with evaporation of the suspension solution, and the suspension solution is preferably circulated through a liquid cooling system.

[0016] Working examples are indicated below, and embodiments of this invention are explained in detail based on these examples. Of course, the description of this application is not restricted to the below listed working examples.

[0017]

[Working Examples]

Working Example 1

First 10.0 g of ground wollastonite (CaSiO_3 , wollastonite) of less than 100 mesh particle size was weighed out and placed in an Erlenmeyer flask. Then 200 mL of distilled water was added, and the mixture was suspended and then placed in an 80°C constant temperature bath. The reaction was carried out for 160 min. by blowing in CO_2 heated to 80°C at a rate of 165 mL per 1 minute. After completion of the reaction, the suspension solution was filtered, and water was removed from the filtrate colloidal precipitate by drying to obtain silica. The obtained silica was observed using an electron microscope.

[0018] Figure 1 of the appended figures is a microscope image of silica (0.1 to 0.5 μm particle size) produced according to this invention. As shown in Figure 1, these particles were near-spherical fine particles of 0.1 to 0.5 μm diameter. Moreover, composition analysis was performed by powder x-ray diffraction of the solids that remained after sufficient evaporation of the moisture of the filtrate solution in a dryer at 110°C. As a result, positions of the diffraction peaks were found to agree with positions of the diffraction lines of calcium carbonate. Moreover, based on gravimetric measurement of the solids, calcium within the raw material substance could be entirely recovered as calcium carbonate.

Working Example 2

First 10.0 g of ground wollastonite of less than 100 mesh particle size was weighed out and placed in an Erlenmeyer flask. Then 200 mL of distilled water was added, and the mixture was suspended. The reaction was carried out for 300 min. by blowing in lime kiln exhaust gas (11.5% CO_2 concentration, 160°C) at a rate of 200 mL per 1 minute. During the reaction, water was fed as required. After completion of the reaction, the suspension solution was filtered, and water was removed from the filtrate colloidal precipitate by drying to obtain silica. The obtained silica was observed using an electron microscope, and composition analysis was performed using the powder x-ray diffraction method. The particles were confirmed to be unreacted wollastonite and fine spherical silica product particles of 0.1 to 0.5 μm diameter.

Comparative Example 1

First 10.0 g of ground wollastonite of less than 100 mesh particle size was weighed out and placed in an Erlenmeyer flask. Then 200 mL of distilled water was added, and the mixture was suspended. Then 100 mL of 0.1 N hydrochloric acid was added, and the reaction was carried out for 1 hr at 70°C. After completion of the reaction, the suspension solution was filtered, and

water was removed from the filtered-out colloidal precipitate by drying to obtain silica. When the obtained silica was observed using an electron microscope, the shape of the silica was found to be irregular with multiple morphologies.

Working Example 3

First 10.0 g of ground sepiolite ($\text{Mg}_5\text{Si}_8\text{O}_{15} \cdot 6\text{H}_2\text{O}$) of less than 100 mesh particle size was weighed out and placed in an Erlenmeyer flask. Then 200 mL of distilled water was added, and the mixture was suspended and then placed in an 80°C constant temperature bath. The reaction was carried out for 160 min. by blowing in CO_2 heated to 80°C at a rate of 165 mL per 1 minute. After completion of the reaction, the suspension solution was filtered using filter paper capable of retaining particles of 10 μm particle size. When composition analysis of the precipitate remaining on the filter paper was carried out by the powder x-ray diffraction method, the precipitate was found to be $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$. Moreover, the colloidal precipitate that passed through the filter paper was re-filtered using filter paper capable of retaining particles of 0.1 μm particle size, and the silica obtained by removal of water contained in the precipitate remaining on the filter paper was observed using an electron microscope.

[0019] Figure 2 of the appended figures is a microscope image of silica produced according to this invention. As shown in Figure 2, the obtained silica particles were near-spherical fine particles of 0.05 to 0.3 μm diameter.

Working Example 4

First 100.0 g of ground sepiolite of less than 100 mesh particle size was weighed out and placed in an Erlenmeyer flask. Then 2000 mL of distilled water was added, and the mixture was suspended and then placed in an 80°C constant temperature bath. The reaction was carried out for 160 min. by blowing in CO_2 heated to 80°C at a rate of 165 mL per 1 minute. After completion of the reaction, the product was separated by filtration per the method of working example 3 as $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ or hydrated silica, respectively. Silica was obtained from the later by removal of water contained in the hydrated silica. When this silica was observed by electron microscope, fine spherical particles were observed of 0.1 to 0.8 μm diameter.

[0020] Despite use of the same reaction temperature and reaction time as that of working example 3, a large quantity of sepiolite was decomposed.

Working Example 5

First 100.0 g of ground sepiolite of less than 100 mesh particle size was weighed out and placed in a gas scrubbing bottle. Then 2000 mL of distilled water and 20 mL of 1 N sodium hydroxide were added, and the mixture was suspended. The mixture was then placed in an 80°C constant temperature bath. The reaction was carried out for 160 min. by blowing in CO_2 heated to 80°C at a rate of 165 mL per 1 minute. After completion of the reaction, the product was separated by filtration per the method of working example 3 as $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ or hydrated silica, respectively. Silica was obtained from the latter by removal of water contained in the hydrated silica. When this silica was observed by electron microscope, fine spherical particles were observed of 0.2 to 1.0 μm diameter.

[0021] Despite use of the same reaction temperature and reaction time as that of working example 3, a large quantity of sepiolite was decomposed.

Comparative Example 2

First 100.0 g of ground sepiolite of less than 100 mesh particle size was weighed out and placed in an Erlenmeyer flask. Then 2000 mL of distilled water and 20 mL of 1 N sodium hydroxide was added, and the mixture was suspended. The reaction was carried out for 1 hr at 100°C. After completion of the reaction, the product was separated by filtration per the method of working example 3 as $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ or hydrated silica, respectively. Silica was obtained from the latter by removal of water contained in the hydrated silica. When the obtained silica was observed using an electron microscope, shape of the silica was found to be irregular with multiple morphologies.

Working Example 6

First 10 g of asbestos ground in a ball mill to less than 100 mesh particle size was weighed out and placed in a gas scrubbing bottle. Then 200 mL of distilled water was added, and the mixture was suspended. The mixture was then placed in an 70°C constant temperature bath. The reaction was carried out for 30 min. by blowing in CO_2 containing 1% SO_2 controlled at 70°C at a rate of 100 mL per 1 minute. Thereafter, the product was separated by filtration per the method of working example 3 as $\text{MgCO}_3 \cdot \text{H}_2\text{O}$ or hydrated silica, respectively. Silica was obtained from the latter by removal of water contained in the hydrated silica. The obtained silica was spherical with a particle size of 0.1 to 1.0 μm .

[0022] As explained previously, the ability of the method of this invention to produce spherical silica is due to blowing of CO_2 into the suspension solution in the fluidized state and reaction between the CO_2 and the substance that contains calcium silicate and/or magnesium silicate. This effectively utilizes the property of CO_2 to dissolve and generate weak acidity. That is to say, the CO_2 dissolves in water and is neutralizing by the substance that contains calcium silicate and / or magnesium silicate. As a result, calcium or magnesium slowly dissolves, and the silicate component mainly becomes a water-dispersed hydrate of silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). Since the reaction proceeds in the fluidized state, the fine amorphous dispersed hydrated silica particles collide in mutually random directions and coalesce. Since the proportion of collisions is the same for any given direction, the dispersed particles grow as spheres. As may be understood from the capillary force of water, surface tension on a convex face has the effect of generating compressive force that is inversely proportional to the radius of curvature of the face. Newly generated fine hydrate of silica attached due to collision with previously grown spherical particles generates a convex face of extremely small radius of curvature on the surface of the spherical particle. Extremely high compressive force acts on this convex face. In order to relieve this force, the substance of this convex part moves toward a surrounding location of high radius of curvature, and radius of curvature of the convex face increases up to the radius of curvature of the spherical particle, and the surface becomes smooth.

[0023]

[Result of the Invention] As explained previously, according to this invention, it is possible to fix CO_2 (considered to be a factor in global warming) with good efficiency using a substance (simple

substance, mixed substance, or solid solution) that contains at least 1 member of a group consisting of calcium silicate and magnesium silicate (present on earth in abundance), and it is simultaneously possible to inexpensively obtain a large quantity of fine spherical silica.

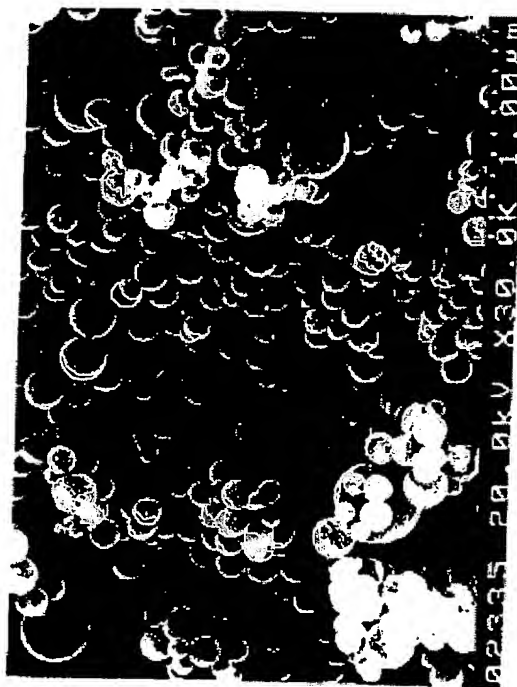
[0024] Furthermore, this invention is capable of utilization for detoxifying treatment of asbestos (chrysotile, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$).

[Simple Description of the Drawings]

[Figure 1] This is a microscope image of silica (0.1 to 0.5 μm particle size) generated during a working example of this invention.

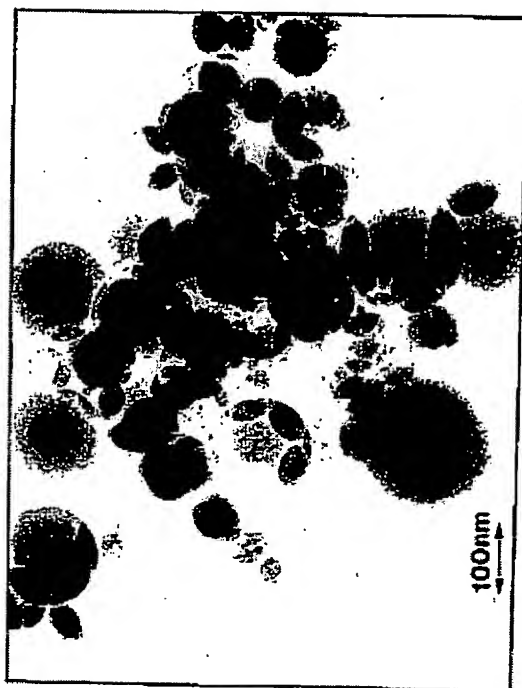
[Figure 2] This is a microscope image of silica (0.05 to 0.3 μm particle size) generated during a working example of this invention.

[Figure 1]



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[Figure 2]



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